Studies on the Extraction and Determination of Metal Salts with Methyl Isobutyl Ketone. XI : Extraction of Thallium

Studies on the Extraction and Determination of Metal Salts with Methyl Isobutyl Ketone. XI Extraction of Thallium*

Hidehiro GOTÔ, Yachiyo KAKITA and Norio ICHINOSE

The Research Institute for Iron, Steel and Other Metals

(Received May 27, 1968)

Synopsis

Liquid-liquid extraction of thallium (III) with methyl isobutyl ketone was studied, employing 10 ml of the solvent and 10 ml of an aqueous solution containing 10 mg of thallium and various mineral acids. The extraction rate was calculated from the amount of thallium salt remaining in the aqueous solution in equilibrium, determined by the oxine method or by photometry. Thallium (III) could be extracted with more than 99.8% recovery from 1.5~8 N hydrochloric acid solutions. The addition of an adequate amount of nitric, sulfuric, or perchloric acid enhanced the extraction up to about 99% even in such a low concentration as 0.5 N hydrochloric acid solution. From the sulfuric acid solution at 8 N only about 21% thallium was extracted.

I. Introduction

The extraction of ionic associated system of thallium from hydrochloric acid solution with organic solvent has been attempted by the use of diethyl ether[1] and of dipropyl ether,[2] the former being of qualitative analysis and the latter being an application of extraction-determination of a trace of thallium in lead. Following the experiments on the extraction of various metal salts with methyl isobutyl ketone,[3-5] the present experiments were carried out on the extraction of thallium from hydrochloric acid solution or from a mixture of hydrochloric acid and other acids, and further, the extraction rate and the extraction conditions were examined.

---

* The **1373rd** report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the J. Chem. Soc. Japan, **88** (1967), 638.

(1) A.A. Noyes, W.C. Bray and E.B. Spear, J.Am. Chem. Soc., **30** (1908), 515, 559.
(2) K. Lounamaa, Z. anal. Chem., **147** (1955), 196.
(3) H. Gotô, Y. Kakita and T. Furukawa, J. Chem. Soc. Japan, **79** (1958), 1513; Sci. Rep. RITU, A-**11** (1959), 1.
(4) H. Gotô and Y. Kakita, J. Chem. Soc. Japan, **79** (1958), 1520; Sci. Rep. RITU, A-**11** (1959), 1.
(5) H. Gotô, Y. Kakita and N. Ichinose, J. Chem. Soc. Japan, **87** (1966), 962; Sci. Rep. RITU, A-**19** (1967), 219.

II. Reagents and apparatus

1. Reagents

Standard thallium solution: A solution of 0.559 g of thallium (III) oxide (Tl_2O_3, 99.9%) dissolved in 75 ml of nitric acid was diluted exactly to 1 *l* with water to prepare a standard stock solution of thallium containing 0.5 mg/ml of Tl (III). This was diluted extemporaneously with 1N nitric acid.

Thallium solution: About 2.8 g of thallium (III) oxide was dissolved in 125 ml of hydrochloric acid and the solution was to 250 ml with water to make a solution containing about 10 mg/ml of Tl (III). A part of this solution was used to determine its concentration photometrically by the 8-hydroxyquinoline (oxine) method[6].

2% oxine solution: 2 g of 8-hydroxyquinoline was dissolved in ethanol to make 100 ml of a solution.

0.2 M sodium acetate solution: 16.4 g of sodium acetate was dissolved in water to make 1 *l* of a solution.

Other acids and salts used were of commercial special grade, and organic solvents used were of commercial first grade.

2. Apparatus

Hitachi photoelectric spectrophotometer Model EPU-2A with 1-cm glass cell, and Hitachi Model EHM-2 glass electrode pH-meter were used.

III. Experimental and result

1. Experimental procedure

A definite quantity of 10 mg of thallium(III) is taken in a 100-ml separatory funnel, hydrochloric acid or a mixture of acids is added, and the solution is diluted with water to 10 ml. To this is added 10 ml of methyl isobutyl ketone and the mixture is shaken for about 30 seconds to effect extraction. When the mixture has separated completely into two layers, the lower aqueous layer is transferred to a 100-ml beaker and the solution is evaporated almost to dryness with a gentle flame. When cooled, 1N nitric acid is added to dissolve the salts and the solution is evaporated to dryness. Thallium is oxidized* by bromine oxidation,[6] and the solution is correctly diluted with 1N nitric acid to bring the solution to a suitable concentration**. A part of this solution is used for photometric determination by the oxine method[6] to determine the quantity of thallium remaining in the aqueous solution and also to determine the extraction rate. The extraction is carried out at the solution temperature of 20°C.

(6) H. Goto, Y. Kakita and N. Ichinose, J. Chem. Soc. Japan, **88** (1967), 640.

* Thallium (III) is liable to undergo pyro-reduction by this heat treatment and should, therefore, be oxidized.

** Thallium (III), 10 ~ 150 μg.

2. Extraction rate of thallium (III) from hydrochloric acid or sulfuric acid solution

Hydrochloric acid solutions of various concentrations containing 8.81 mg of thallium (III) were prepared and the extraction rate was calculated from the experimental procedure outlined in III-1. The results are shown by Curve I in Fig. 1, which indicates that a high extraction rate over 99.8% can be obtained by the use of 1.5～8 N hydrochloric acid***. In the concentration range of 1～3 N hydrochloric acid, the mixture with organic solvent tends to form an emulsion, while it separates rapidly and clearly into the two layers in a concentration range of 4～7 N hydrochloric acid. Above 8N, the separation is indistinct and the volume of organic layer diminishes. At the concentration of hydrochloric acid above 9N, the separation does not take place.

Examination of the extraction from sulfuric acid by the same procedure showed, as indicated by Curve II in Fig. 1, that only about 21% of thallium (III) was extracted in sulfuric acid concentration of 8N, and that the organic layer colored yellowish brown when 10N sulfuric acid was used.

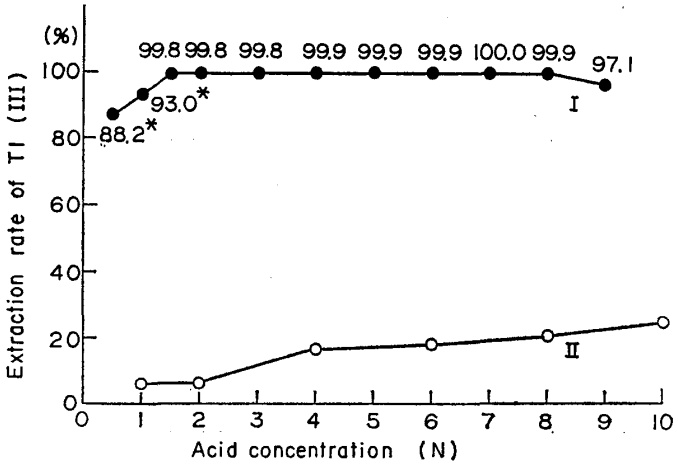

Fig. 1. Extraction rate of Tl (III)
I : Tl(Ⅲ)-HCl[Tl(Ⅲ) : 8.81 mg]
Ⅱ : Tl(Ⅲ)-H_2SO_4[Tl(Ⅲ) : 10.04 mg]
* Extraction rate of Tl(III) from organic layers.

3. Effect of other acids

The effect of the presence of nitric, sulfuric, or perchloric acid at the time of extraction of thallium from hydrochloric acid solution was examined. Nitric, sulfuric, or perchloric acid was added to 0.5, 2, or 5N hydrochloric acid solution

*** In the case of hydrochloric acid below 4 N, the organic layer extracted was analyzed at the same time to obtain the extraction rate which was compared with that obtained from the aqueous layer. In the range of 1.5～4 N hydrochloric acid, approximately agreeing results were obtained. In other concentrations, the extraction rate obtained by analysis of the organic layer gave lower values, being 6.8% at 1.0 N, 11.5% at 0.5N, and 12.7% at 0.25 N hydrochloric acid.

Table 1. Effect of other acids on extraction.

Kind of acid	Concn. of acid (N)	Tl (III) remained		Tl (III) extracted	
		(mg)	(%)	(%)	mean (%)
HCl	0.5*	—	—	88.2	88.2
		—	—	88.2	
	2	0.020	0.2	99.8	99.8
		0.020	0.2	99.8	
	5	0.012	0.1	99.9	99.9
		0.011	0.1	99.9	
$HCl+HNO_3$	0.5+2	0.075	0.9	99.1	99.2
		0.064	0.7	99.3	
	0.5+4	0.067	0.8	99.2	99.2
		0.066	0.8	99.2	
	2+2	0.018	0.2	99.8	99.8
		0.020	0.2	99.8	
	5+2	0.002	0.0	100.0	100.0
		0.000	0.0	100.0	
$HCl+H_2SO_4$	0.5+2	0.082	0.9	99.1	99.1
		0.084	1.0	99.0	
	0.5+4	0.114	1.3	98.7	98.7
		0.118	1.3	98.7	
	0.5+6	0.093	1.1	98.9	99.0
		0.089	1.0	99.0	
	2+2	0.000	0.0	100.0	100.0
		0.001	0.0	100.0	
	5+2	0.000	0.0	100.0	100.0
		0.000	0.0	100.0	
$HCl+HClO_4$	0.5+2	0.078	0.9	99.1	99.1
		0.082	0.9	99.1	
	0.5+4	0.066	0.8	99.2	99.2
		0.070	0.8	99.2	
	2+2	0.015	0.2	99.8	99.9
		0.012	0.1	99.9	
	5+2	0.004	0.1	99.9	99.9
		0.005	0.1	99.9	

Tl (III) : 8.81 mg.
*Extraction rate of Tl (III) from organic layers.

in the ratio of 2, 4, or 6N, and the extraction was carried out by the procedure outlined in III-1.

As shown in Table 1, the addition of other acids in the ratio of 2, 4, or 6N to hydrochloric acid of a low concentration, such as 0.5N, resulted in a high extraction rate of about 99%, indicating that the addition of these acids would increase the extraction rate.